Renewable and Sustainable Energy Reviews 14 (2010) 955–970

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

High-temperature phase change materials for thermal energy storage

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ARTICLE INFO

Article history:
Received 28 October 2009
Accepted 2 November 2009

Keywords:
Heat storage materials (HSMs)
Phase change materials (PCMs)
Latent heat storage
Thermal energy storage (TES)
Salt mixes and compositions
Metal alloys
Thermophysical properties
Corrosion

ABSTRACT

The development of energy saving technologies is very actual issue of present day. One of perspective directions in developing these technologies is the thermal energy storage in various industry branches. The review considers the modern state of art in investigations and developments of high-temperature phase change materials perspective for storage thermal and a solar energy in the range of temperatures from 120 to 1000 °C. The considerable quantity of mixes and compositions on the basis of fluorides, chlorides, hydroxides, nitrates, carbonates, vanadates, molybdates and other salts, and also metal alloys is given. Thermophysical properties of potential heat storage salt compositions and metal alloys are presented. Compatibility of heat storage materials (HSM) and constructional materials have found its reflection in the present work. Data on long-term characteristics of some HSMs in the course of repeated cycles of fusion and solidification are analyzed. Article considers also other problems which should be solved for creation of commercial high-temperature heat storage devices with use of phase change materials.

Contents

1. Introduction

Last 30 years were characterized by essential increase in consumption of energy. It has led to substantial growth in atmosphere of greenhouse gases and, as consequence, to climatic changes. Last circumstance, also as well as a constant rise in prices for energy carriers promoted comprehension of necessity of more effective utilization of energy in all spheres of human activity. The governments of many countries stimulate as development energy saving technologies in traditional branches of economy, and development of the technologies based on use of noncombustible renewable energy sources. Thermal energy storage plays significant role in developing the specified technologies.

Storage is a key element to improve the efficiency of thermal energy utilization in various branches of economy. Scale use of solar energy assumes also its wider storage. Systems of storage of

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1364-0321/$ – see front matter
doi:10.1016/j.rser.2009.11.011

Nomenclature

T	temperature, °C or (K)
C_p	thermal capacity (J/g K)
ΔH	heat of fusion (J/g)
wt.%	weigh percent
mol.%	molar percent

Greek letters

ρ	density (g/cm^3)
λ	thermal (heat) conductivity (W/m K)

Subscripts

m	melting
l	liquid
s	solid
sol	solidification

thermal energy are characterized by a variety of levels of working temperatures, capacities and used heat transfer carriers and that fact, that each heat store differs in the specific parameters. Therefore along with the decision of the problems connected with methods and the ways of storage of thermal energy, designing heat storage devices and their integration into a production cycle, research and development of perspective heat storage materials has the prime value.

To store thermal energy the sensible or latent heat storage materials are widely used. However, rather low thermal capacity of sensible heat storage materials leads to considerable volumes heat storage units (HSU). Therefore last decades the researchers place emphasis on phase change materials (PCM) in which heat storage is carried out due to latent heat of fusion. Application such PCMs allows to lower the volume of HSU essentially. Low temperature PCMs became objects of prime investigations in this area. In the middle of the eightieth years of last century, the results of basic investigations have been generalized in [1–3]. Various aspects of investigations, developments and applications in low temperature PCMs have found their reflection in the subsequent reviews and monographies [4–30]. The field of PCMs' applications is not limited to low temperatures (about 120 °C) only.

According to [30], 5–6% of the energy consumed annually in Germany is applied in temperature interval 100–300 °C. This energy is used for steam generation at low temperatures and moderate pressure in the food and textile industry, in production of cardboard and paper, building materials, rubber, etc. Expansion in electricity production on solar thermal power stations demands developing HSUs with high reliability and thermal efficiency, and low cost. Utilization of heat stores with high-temperature PCMs for the above-mentioned applications, as many researchers and experts believe, will allow raising considerably efficiency in using the thermal and solar energy.

Gasanaliev and Barataeva [31] generalized the results of works of the Russian and some foreign researchers in studying some perspective salt and metal melts, which can be used as high-temperature PCMs. This review did not consider many foreign researches till 2000, and also the publications which have appeared after publication of the review. The present review analyses the state of studies and developments of PCMs, which can be used to store thermal and solar energy in the range of 120–1000 °C.

The basic requirements imposed upon phase change heat storage materials have been formulated in [5,25,32]. These materials should possess following properties:

- the demanded melting temperature, which provides operating the storage unit in a desirable interval of working temperatures;
- high specific thermal capacity, heat of fusion and density to provide the minimum sizes of the HSU;
- congruent melting: PCMs should keep stoichiometric composition in solid and liquid conditions. Otherwise distinction in density of the liquid and solid phase, appeared at fusion, will lead to separation of phases, and, hence, change stoichiometric composition of melt;
- reliable convertibility at repeated phase transformations;
- high heat conductivity providing the minimum temperature gradients, demanded for charging and discharging HSU;
- the minimum change in volume at transition from one phase in another, that allow us to use simple forms of containers and heat exchangers;
- insignificant overcooling during hardening;
- chemical stability providing demanded life time of the HSU;
- compatibility and resistance to oxidation with constructional materials;
- they must be nontoxic or a little toxic;
- flame and fire safety;
- availability and cheapness.

Development and producing the commercial HSUs are rather labor-consuming and long-term process demanding attraction of board circle of scientists and experts of various specialties. Fig. 1 presents the basic stages of works, which should be solved to let out on the market such a commercial product as HSU on the basis of phase change materials.

2. Salts and salt compositions

2.1. Choice of salts and salt compositions to be perspective for heat storage

From the requirements imposed upon phase change heat storage materials (HSM), it is seen, that they, first of all, should has suitable melting temperature and, whenever possible, high heat of fusion. In a considered interval of temperatures, the great interest represent the inorganic salts, the melting temperature of which lays in the range from 250 to 1680 °C, and heat of fusion from 68 to 1041 J/g. Table 1 gives the basic group of salts that serve as origin materials to develop perspective HSM intended for work in the field of high temperatures.

Pure salts as it is seen from this table have rather a heat of fusion that essentially reduces area of their application in technological processes. Therefore efforts of researchers, first of all, have been concentrated to expansion of a temperature interval at simultaneous decrease in temperatures of fusion of HSM. The most perspective compositions which meet targets in view double and ternary eutectics were considered. High heat of fusion of fluorides and chlorides, and also low cost of the latter stimulated the studies of double and ternary systems on the basis of fluorides and chlorides. Eutectic compositions on the basis of fluorides and chlorides which were offered by different researchers as phase change HSMs are presented in Tables 2 and 3.

Besides fluorides and chlorides, the compositions on the basis hydroxides, nitrates, carbonates and other salts represent the considerable interests (see Tables 4 and 5). Compositions on the basis of double and ternary eutectics are based on the studies spent, mainly, till seventieth and eightieth years of last century. As it is seen from Tables 2 and 3, the goal-seeking investigations and developments of researchers from the Samara state university, Dagestan and other scientific centers in Russia have shown perspectives quaternary and quinary compositions on a basis molybdates, vanadates and sulphates.

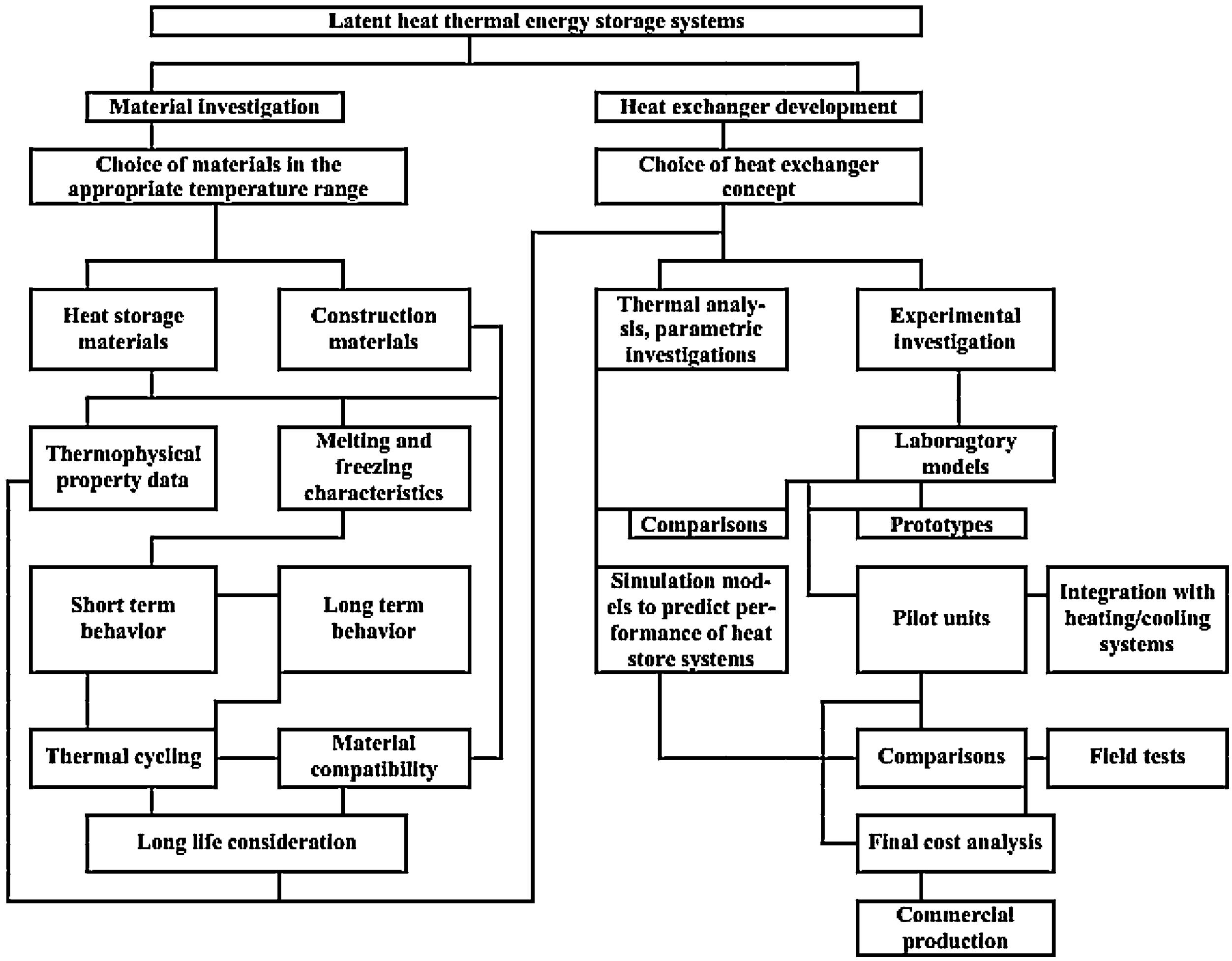


Fig. 1. Flowchart providing an overview of the various steps in the development of a latent heat storage system [32].

2.2. Thermophysical properties of salts and salt compositions

Following stage in designing and creation HSU is studying the thermophysical properties of phase change HSMs. Investigation of thermophysical properties of substances is rather labor-intensive process and it is naturally not lags behind developing the new materials. Data on thermophysical properties are scattered under many handbooks and magazines, which, frequently, are not accessible to a wide range of experts. It concerns as well salts and compositions on their basis. There is not enough publications

Table 1
Melting temperatures and heat of fusion of some salt [33].

Metal	Fluioride	Chloride	Bromide	Iodide	Sulphate	Nitrate	Carbonate	Chromate	Molybdate	Tungstate
Melting temperature, °C										
Lithium	849	610	550	469	858	253	732	485	703	740
Sodium	996	801	742	661	884	307	858	794	688	696
Potassium	858	771	734	681	1069	335	900	973	926	923
Rubidium	795	723	692	556	1070	312	873	994	955	952
Cesium	703	645	638	632	1015	409	793	975	935	953
Magnesium	1263	714	711	633	1137	426	990		1230	826
Calcium	1418	772	742	783	1460	560	1330	1000	1449	1580
Strontium	1477	875	657	538	1605	645	1490	1283	1457	1535
Barium	1368	961	857	711	1680	594	1555	1444	1458	1475
Heat of fusion, J/g										
Lithium	1041	416	203		84	373	509	168	281	157
Sodium	794	482	255	158	165	177	165	146	109	107
Potassium	507	353	215	145	212	88	202	41	163	86
Rubidium	248	197	141	104	145	31			140	78
Cesium	143	121	111	96	101	71		94	75	63
Magnesium	938	454	214	93	122		698			
Calcium	381	253	145	142	203	145				
Strontium	226	103	41	57	196	231				
Barium	105	76	108	68	175	209				

Table 2
Fluoride salt compositions.

Salt composition (mol.%)	T_m, °C	ΔH_f, J/g	Reference
NaF(5)–87NaNO$_3$–8NaCl	288	224	[34]
LiF(7.0)–41.5LiCl–16.4LiVO$_3$–35.1Li$_2$CrO$_4$	340	177	[35]
LiF(16.2)–42.0LiCl–17.4LiVO$_3$–11.6Li$_2$SO$_4$–11.6Li$_2$MoO$_4$	363	284 ± 7	[36]
LiF(16.2)–51.5LiCl–16.2Li$_2$SO$_4$–16.2Li$_2$MoO$_4$	402	291	[37]
LiF(17.6–17.7)–(33.2–33.8) KF–(40.0–40.4) KCO$_4$–(8.6–8.7) KCl[a]	422–426	407–412	[38]
LiF(20)–80LiOH	427	1163	[39]
LiF(25.0)–43.8LiVO$_3$–14.8Li$_2$SO$_4$–16.5Li$_2$MoO$_4$	428	260	[40]
LiF(80)–20LiOH	430	528	[41]
LiF(45.7)–1.8BaF$_2$–41.2KF–11.3NaF	438	332	[41]
LiF(42.5–45.5)–(41.0–43.0) KF–(10.7–11.5) NaF–(2.8–3.0) KCl	440–448	682–692	[42]
LiF(27.1)–11.9NaF–55.1KF–5.9MgF$_2$[a]	449	699	[43]
LiF(29.2)–11.7NaF–59.1KF[a]	454	414	[43]
LiF(46.5)–42KF–11.5–NaF	454	325	[41]
Li(29)–12NaF–59KF[a]	463	442	[44]
LiF(73.6)–26.4LiCl	485	403	[41]
KF(50)–50LiCl	487	344	[41]
LiF(33)–67KF[a]	493	458	[44]
LiF(18.0)–53.0LiVO$_3$–29.0Li$_2$MoO$_4$	493	297	[45]
NaF(20.1)–79.9ZrF$_4$[a]	510	255	[43]
NaF(17)–21KCl–62K$_2$CO$_3$[a]	520	274	[46,47]
KF(23)–40KCl–37K$_2$CO$_3$[a]	528	283	[46,47]
LiF(36.1)–34NaF–18.5CaF$_2$–3.3BaF$_2$–8.1BaMoO$_4$	536	653	[48]
KF(40)–60KBr	576	315	[49]
LiF(25.67–25.76)–(36.45–36.57)NaF–(27.0–27.25) CaF$_2$–(10.63–10.67)MgF$_2$[a]	593–595	510–515	[50]
KF(55)–45KCl	605	407	[49]
LiF(35.2)–38.3NaF–26.5CaF$_2$	615	636	[43]
LiF(52)–35NaF–13CaF$_2$	615	640	[39]
Li(46)–44NaF–10MgF$_2$	632	858	[39]
NaF(27)–73NaBr	642	360	[51]
LiF(34.51–34.79)–(37.25–37.6)MgF$_2$–(24.5–25.0)CaF$_2$–(3.21–3.31)NaF	651–657	460–470	[52]
LiF(60)–40NaF	652	816	[39]
NaF(33.5)–66.5NaCl	675	572	[51]
LiF(62)–19NaF–19MgF$_2$	693	690	[53,54]
LiF(70)–30MgF$_2$	728	520	[53,54]
NaF(65)–23CaF$_2$–12MgF$_2$	743	568	[55]
LiF(67)–33MgF$_2$	746	947	[39]
LiF(74)–13KF–13MgF$_2$	749	860	[53,54]
LiF(80)–20CeF$_3$	756	500	[53,54]
LiF(81.5)–19.5CaF$_2$	769	820	[53,54]
KF(85)–15CaF$_2$	780	440	[53,54]
KF(85)–15MgF$_2$	790	520	[53,54]
NaF(64)–20MgF$_2$–16KF	804	650	[50,51]
NaF(62.5)–22.5MgF$_2$–15KF	809	543	[39,55]
NaF(68)–32CaF$_2$	810	600	[53,54]
NaF(75)–25MgF$_2$	832	627	[39,55]
CaF$_2$(49)–41.4CaSO$_4$–9.6CaMoO$_4$	943	237	[56]

[a] wt.%.

generalizing thermophysical properties of high-temperature PCMs. Below we will consider only those publications that could find on a question interesting for us.

In 1977–1978, Marianovski and Maru with colleagues from the Chicago Institute of Gas Technology published the results of investigations of various aspects of phase change heat storage systems working above 450 °C. In particular, they have generalized the data on thermophysical properties that are presented in Table 6. Unfortunately, these researchers have not specified temperatures, at which measurements were carried out. And consequently, the data specified in Table 6 can be considered as approximate data.

Venkatesetti and LeFrois [58] from Honeywell, Inc. studying thermal storage materials intended for storage units in solar thermal power stations have found in the literature nine inorganic eutectic compositions with melting points between 220 and 290 °C. Thermophysical properties of nine salt mixes, measured by these authors with using a method of differential-scanning calorimetry, are presented in Table 6. The thermal capacity was

Table 3
Chloride eutectic compositions.

Salt composition (mol.%)	T_m, °C	ΔH_f, J/g	Reference
LiCl(28.5–28.9)–(43.5–44.5)CsCl–(13.7–14.1)KCl–(13.3–13.5)RbCl	256 ± 2.5	375–380	[57]
LiCl(59.15)–40.85Ca(NO$_3$)$_2$	270	167	[58]
NaCl(7.8)–85.8NaOH–6.4NaCO$_3$	282	316	[39]
NaCl(8)–5NaF–87NaNO$_3$	288	224	[34]
LiCl(54.2)–6.4BaCl$_2$–39.4KCl	320	170	[41]
LiCl(41,5,0)–16.4LiVO$_3$–7.0LiF–11.6Li$_2$SO$_4$–35.1Li$_2$CrO$_4$	340	177	[35]
LiCl(47.4–47.7)–(46.8–47.0)KCl–(3.2–3.4)LiCO$_3$–(2.1–2.4)LiF[a]	340–343	375–380	[59]
LiCl(58)–42KCl	348	170	[41]
KCl(28.7)–45MnCl$_2$–26.3NaCl	350	215	[57]
KCl(45.5)–34.5MnCl$_2$–20NaCl	390	230	[57]
LiCl(23.4–24.2)–(24.8–25.3) LiVO$_3$–(27.1–27.6)Li$_2$MoO$_4$–(17.3–17.8)Li$_2$SO$_4$–(6.1–6.2)LiF[a]	360–363	278–284	[60]
LiCl(42.0)–17.4LiVO$_3$–17.4LiF–11.6Li$_2$SO$_4$–11.6Li$_2$MO$_4$	363	284 ± 7	[36]
NaCl(22.5–26.5)–(18.5–22.5) KCl–(57.0–53.0) MgCl$_2$[a]	385–393	405–410	[61]
KCl(21.6)–45.4MgCl$_2$–33.0NaCl	385	284	[57]
KCl(20)–50MgCl$_2$–30NaCl	396	291	[57]
KCl(22)–51MgCl$_2$–27NaCl	396	290	[57]
KCl(37.7)–37.3MnCl$_2$–25NaCl	400	235	[57]
LiCl(51.5)–16.2LiF–16.2Li$_2$SO$_4$–16.2Li$_2$MoO$_4$	402	291	[37]
NaCl(56)–44MgCl$_2$	430	320	[57]
KCl(54)–46ZnCl$_2$[a]	432	218	[46,47]
KCl(61)–39MgCl$_2$[a]	435	351	[46,47]
NaCl(56.2)–43.8MgCl$_2$	442	325	[57]
LiCl(58.5)–23.6Li$_2$SO$_4$–17.9Li$_2$MoO$_4$	445	327	[62]
KCl(36)–64MnCl$_2$	448	236	[57]
LiCl(49.0)–12.75Li$_2$SO$_4$–38.25LiVO$_3$	449	450	[63]
KCl(35)–65MnCl$_2$	450	237	[57]
NaCl(60)–40MgCl$_2$	450	328	[57]
NaCl(48)–52MgCl$_2$[a]	450	430	[46,47]
CaCl$_2$(47.6)–8.1KCl–41.3NaCl–2.9NaF	460	231	[57]
CaCl$_2$(41.6)–2.2KCl–8.8MgCl$_2$–47.4NaCl	460	245	[57]
CaCl$_2$(50)–7.25KCl–42.75NaCl	465	245	[57]
KCl(36)–64MgCl$_2$[a]	470	388	[46,47]
BaCl$_2$(8.7)–52.3KCl–18.2MgCl$_2$–20.7NaCl	475	248	[57]
BaCl$_2$(13.1)–16.9CaCl$_2$–47.3KCl–22.7NaCl	478	208	[57]
BaCl$_2$(9.3)–22.2CaCl$_2$–42.7KCl–25.8NaCl	479	217	[57]
LiCl(69.5)–26.5LiF–4MgF$_2$	484	157	[64]
CaCl$_2$(50)–1.5CaF$_2$–48.5NaF	490	264	[57]
CaCl$_2$(52.3–55)–(45–47.2) NaCl	490–500	233–239	[57]
CaCl$_2$(52.8)–47.2NaCl	500	239	[57]
NaCl(33)–67 CaCl$_2$[a]	500	281	[46,47]
MgCl$_2$(37)–63 SrCl$_2$[a]	535	239	[46,47]
KCl(25)–27 CaCl$_2$–48 MgCl$_2$[a]	487	342	[46,47]
CaCl$_2$(66)–5KCl–29NaCl[a]	504	279	[46,47]
SrCl$_2$(68)–13KCl–19NaCl[a]	504	223	[46,47]
KCl(21)–17NaF–62K$_2$CO$_3$[a]	520	274	[46,47]
NaCl(5)–40NaBr–55Na$_2$MoO$_4$	524	215	[49]
KCl(40)–23KF–37K$_2$CO$_3$[a]	528	283	[46,47]
KCl(28)–19NaCl–53BaCl$_2$[a]	542	221	[46,47]
KCl(24)–47BaCl$_2$–29CaCl$_2$[a]	551	219	[46,47]
NaCl(952)–48NiCl$_2$	573	558	[39]
LiCl(94.5)–5.5MgF$_2$	573	131	[64]
KCl(45)–55KF	605	407	[65]
NaCl(38.5)–23NaBr–38.5Na$_2$MoO$_4$	612	168	[66]
CaCl(38.5)–11CaSO$_4$–4CaMoO$_4$	673	224	[67]

[a] wt.%.

Table 4
Hydroxides and nitrates compositions.

Salt composition (mol.%)	T_m, °C	ΔH_f, J/g	Reference
Hydroxides			
NaOH(50)–50KOH	169–171	202–213	[68]
LiOH(30)–70NaOH	210–216	278–329	[68]
NaOH(20)–80$NaNO_2$	230–232	206–252	[60]
NaOH(73)–27$NaNO_2$	237–238	249–295	[60]
NaOH(78.1)–3.6NaCl–18.3$NaNO_3$	242	242	[60]
NaOH(28)–72$NaNO_3$	246–247	182–257	[60,68]
NaOH(55.6)–4.2NaCl–40.2$NaNO_3$	247	213	[60]
LiOH(63)–37LiCl	264	437	[39]
NaOH(59)–41$NaNO_3$	266	278	[69]
LiOH(65.5)–34.5LiCl	274	339	[41]
LiOH(62)–36.5LiCl–1.5KCl	282	300	[41]
NaOH(81.5)–18.5$NaNO_3$	256–258	251–292	[60,69]
NaOH(59)–41$NaNO_3$	266	221	[60]
NaOH(85.8)–7.8NaCl–6.4Na_2CO_3	282	316	[39]
NaOH(88.3)–5.3NaCl–6.4Na_2CO_3	282	279	[60]
NaOH(87.3)–6.1NaCl–6.6Na_2CO_3	291	283	[60]
NaOH(85.8)–7.8NaCl–6.4Na_2CO_3	298	286	[60]
NaOH(77.2)–16.2NaCl–6.6Na_2CO_3	318	290	[60]
LiOH(80)–20LiF	427	1163	[39]
Nitrates			
$LiNO_3$(29)–17$NaNO_3$–49.4KNO_3–4.6$Sr(NO_3)_2$[a]	105	110	[31]
$LiNO_3$(33)–67KNO_3[a]	133	170	[29]
$LiNO_3$(31.7)–68.3KNO_3[a]	135	136	[31]
KNO_3(53)–40$NaNO_2$–7$NaNO_3$[a]	142	80	[29]
$LiNO_3$(55.4)–4.5$NaNO_3$–40.1KCl[a]	160	266	[31]
$LiNO_3$(58.1)–41.9KCl[a]	166	272	[31]
$LiNO_3$(47.9)–1.4LiCl–50.7$NaNO_3$[a]	180	265	[31]
$LiNO_3$57)–43$NaNO_3$[a]	193	248	[31]
$LiNO_3$(49)–51$NaNO_3$[a]	194	265	[29]
$LiNO_3$(45)–47$NaNO_3$–8$Sr(NO_3)_2$[a]	200	199	[31]
$LiNO_3$(87)–13NaCl[a]	208	369	[31]
KNO_3(54)–46$NaNO_3$[a]	222	100	[29]
$NaNO_3$(54)–46KNO_3	222	117	[58]
$NaNO_3$(18.3)–3.6NaCl–78.1NaOH	242	242	[60]
$NaNO_3$(40.2)–4.2NaCl–55.6NaOH	247	213	[60]
$NaNO_3$(70)–30NaOH	247	158	[58]
$LiNO_3$(97.4)–2.6$Ba(NO_3)_2$	253	368	[58]
$LiNO_3$(93.6)–6.4NaCl[a]	255	354	[31]
$Ca(NO_3)_2$(40.85)–59.15LiCl	270	167	[58]
NaNO3(86.3)–8.4NaCl–5.3Na_2SO_4	287	177	[58]

[a] wt.%.

Table 5
Salt compositions on the basis of carbonates and some other salts.

Salt composition (wt.%)	T_m, °C	ΔH_f, J/g	Reference
Na_2CO_3(6.4)–85.8NaOH–7.8NaCl	282	316	[39]
Li_2CO_3(32.1)–34.5K_2CO_3–33.4Na_2CO_3	397	276	[46,47]
Li_2CO_3(47)–53K_2CO_3	488	342	[46,47]
Li_2CO_3(47)–53K_2CO_3	491	321	[44]
Li_2CO_3(46.6)–53.4K_2CO_3	488	391	[70]
Li_2CO_3(44)–56Na_2CO_3	496	370	[46,47]
Li_2CO_3(28)–72K_2CO_3	498	263	[46,47]
Li_2CO_3(28.5)–71.5K_2CO_3	498	316	[70]
Li_2CO_3(44.3)–55.7Na_2CO_3	498	393	[70]
Li_2CO_3(35)–65K_2CO_3	505	344	[46,47]
Li2CO3(32)–35K_2CO_3–33Na_2CO_3	397	276	[46,47]
K_2CO_3(62)–17NaF–21KCl	520	274	[46,47]
K_2CO_3(37)–40KCl–23KF	528	283	[46,47]
Li_2CO_3(20)–60Na_2CO_3–20K_2CO_3	550	283	[46,47]
Li_2CO_3(22)–16Na_2CO_3–62K_2CO_3	550	288	[46,47]
K_2CO_3(47.8)–52.2K_2CO_3	710	176	[70]
K_2CO_3(50)–50Na_2CO_3	710	163	[70]
K_2CO_3(51)–49Na_2CO_3	710	163	[46,47]
NaBr(43)–2NaF–55Na_2MoO_4[a]	506	241	[49]
Li_2SO_4(59.8)–36.7Li_2MoO_4–3.5$CaMoO_4$[a]	538	406	[71]
KBr(60)–40KF[a]	576	315	[49]
KBr(65)–35K2MoO4[a]	625	90.5	[72]
Li_2SO_4(82)–11.44$CaSO_4$–6.56$CaMoO_4$[a]	680	207	[49]

[a] mol.%.

measured in the area covering 25 °C below melting point and 25 °C above melting point. The data specified in the table on thermal capacity are the average values found for solid and liquid states.

Some thermal properties of salt compositions, which Birchenall and Riechman [73] found in the literature, are summarized in Table 7.

The Japanese researcher Kamimoto [74] of Electrotechnical laboratory in Ibaraki used twin type of drop calorimeter to determine the heat of fusion of such salts as $LiNO_3$ and $NaNO_2$. The calorimeter was preliminary calibrated with sapphire. Heat of fusion of lithium nitrate is to be equal 357 J/g, and sodium nitrite, 222 J/g. According to the author, the measurement error does not exceed 1.5%.

Takahashi et al. [68] investigated properties of the hydroxides of lithium, sodium and potassium. Measurements have been made on high-precision differential-scanning calorimeter Perkin-Elmer DSC-2. The heat of fusion has been determined with using a method suggested by Takahashi earlier in [75]. In view of corrosion activity and wettability of hydroxides, it was impossible to use containers of aluminum, platinum or quartz. The polytetrafluoroethylene (teflon) is used as container. New samples of teflon have shown their suitability for measurement of heat of fusion and thermal capacities of salts. The error of measurements with such containers was less than 2%. Because of phase transformations and melting of teflon (nearby 290, 300 and 600 K correspondingly) thermoanalytical studies were limited to an interval of temperatures from 323 and 573 K. The thermal capacity of sodium hydroxide is described by the following regression equation:

$$C_{ps}(\mathrm{J/g\,K}) = 1.028 + 1.443 \times 10^{-3}\,T(\mathrm{K}) \quad \text{for } 330-505\,\mathrm{K}$$

For equimolar eutectic blend of NaOH and KOH (50:50 mol.%) the results of measurements of thermal capacity are described by the following regression equations:

$$C_{ps}(\mathrm{J/g\,K}) = 0.905 + 1.124 \times 10^{-3}\,T(\mathrm{K}) \quad \text{for } 330-360\,\mathrm{K}$$
$$C_{ps}(\mathrm{J/g\,K}) = 0.435 + 2.451 \times 10^{-3}\,T(\mathrm{K}) \quad \text{for } 365-430\,\mathrm{K}$$
$$C_{ps}(\mathrm{J/g\,K}) = 1.800 + 0.023 \times 10^{-3}\,T(\mathrm{K}) \quad \text{for } 470-575\,\mathrm{K}$$

The melting point of the blend lies in the range of 169–171 °C, heat of fusion is found to be equal 202–213 J/g. The lower values of the specified values correspond to the data received from curves of heating, and higher values—from cooling curves.

For eutectic compositions of LiOH and NaOH (30:70 mol.%) the following equations have been offered:

$$C_{ps}(\mathrm{J/g\,K}) = 0.772 + 2.81 \times 10^{-3}T(\mathrm{K}) \quad \text{for } 330-450\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 2.020 + 1.54 \times 10^{-3}T(\mathrm{K}) \quad \text{for } 510-575\,\mathrm{K}$$

The melting temperature of the composition is found to be equal 215–216 °C, and heat of fusion was within 278–290 J/g. The composition undergoes a phase transformation at 173–187 °C, with thermal effect of 54–58 J/g.

In 1988, Takahashi et al. [76] had been published results of measurements of thermal capacities and heat of fusion of nitrates of lithium, sodium and potassium and some compounds and mixes on their basis. The found value of heat of fusion for lithium nitrate was 363, for sodium nitrate 173, and for potassium nitrate 96.6 J/g. Heat of phase transformation in solid state for sodium nitrate is equal 45, and for potassium nitrate 50.6 J/g. The measured values of melting temperatures and solidification temperature, and also heat of fusion are presented in Table 8. It is easy to notice, that for some compounds and compositions the considerable variations in melting temperatures and solidification temperatures are registered. The reasons of such a variation are not established. Thermal capacity measurements have yielded following results:

Table 6
Thermophysical properties of some salt compositions extracted from [46,47].

Composition, wt.%	T_m, °C	ΔH_f, J/g	C_p, J/gK		λ, W/m K	ρ_s at 25 °C, g/cm^3	Safety (d)	Compatibility	Price, US$/kg
			Solid	Liquid	Liquid				
$KCl(54)–46ZnCl_2$	432	218	0.67	0.88	0.83	2.41	2e	SS	0.59
$KCl(61)–39Mg Cl_2$	435	351	0.80	0.96	0.81	2.11	2e	SS	0.13
$NaCl(48)–52MgCl_2$	450	430	0.92	1.00	0.95	2.23	2	SS	0.18
$KCl(36)–64MgCl_2$	470	388	0.84	0.96	0.83	2.19	2e	SS	0.20
$NaCl(33)–67CaCl_2$	500	281	0.84	1.00	1.02	2.16	1	SS	0.07
$MgCl_2(37)–63SrCl_2$	535	239	0.67	0.80	1.05	2.78	2	SS	0.73
$Li_2CO_3(47)––53K_2CO_3$	488	342	1.03	1.34	1.99	2.20	2	SS	1.04
$Li_2CO_3(44)–556Na_2CO_3$	496	370	1.80	2.09	2.09	2.32	2	SS	0.77
$Li_2CO_3(28)–72K_2CO_3$	498	263	1.46	1.80	1.85	2.24	2	SS	0.79
$K_2CO_3(51)–49Na_2CO_3$	710	163	1.67	1.56	1.73	2.40	2	SS	0.24
LiF(33)–67KF	442	618	1.34	1.63	3.98	2.53	3e	316 SS	2.67
$NaF(67)–33MgF_2$	832	616	1.42	1.38	4.65	2.14	3e	316 SS	1.26
$NaBr(45)–55MgBr_2$	431	212	0.50	0.59	0.90	3.49	2e	316 SS	3.57
LiF(20)–80LiOH	426	869	0.88	1.00		1.60	3	300 SS	4.54
$KCl(25)–27CaCl_2–48MgCl_2$	487	342	0.80	0.92	0.88	2.53	2e	SS	0.18
$KCl(5)–29NaCl–66CaCl_2$	504	279	1.17	1.00	1.00	2.15	2e	SS	0.07
$KCl(13)–19NaCl–68SrCl_2$	504	223	0.67	0.84	1.05	2.75	2e	SS	3.02
$KCl(28)–19NaCl–53BaCl_2$	542	221	0.63	0.80	0.86	3.02	2e	SS	0.20
$KCl(24)–47BaCl_2–29CaCl_2$	551	219	0.67	0.84	0.95	2.93	2e	SS	0.20
$Li_2CO_3(32)–35K_2CO_3–Na_2CO_3$	397	276	1.67	1.63	2.02	2.30	2	SS	0.73
NaF(12)–59KF–29LiF	454	590	1.34	1.55	4.50	2.53	3e	316 SS	2.45
$KCl(40)–23KF–37K_2CO_3$	528	283	1.00	1.26	1.19	2.28	3e	SS	0.51
$NaF (17)–21KF–62K_2CO_3$	520	274	1.17	1.38	1.50	2.38	3e	SS	0.40
$Li_2CO_3(35)–65K_2CO_3$	505	344	1.34	1.76	1.89	2.26	2	SS	0.88
$Li_2CO_3(20)–60Na_2CO_3–20K_2CO_3$	550	283	1.59	1.88	1.83	2.38	2	SS	0.46
$Li_2CO_3(22)–16Na_2CO_3–62K_2CO_3$	580	288	1.80	2.09	1.95	2.34	2	0.66	

d, toxic hazard rating code: 2, moderate; 3, high; e, when strongly heated, they emit high toxic fumes; SS, stainless steel.

Table 7
Thermophysical properties of some salts compositions [73].

Composition, wt.%	T_m, °C	ΔH_f, J/g	ρ, g/cm^3	C_{ps}, J/gK	λ_s W/m K
$NaF(75)–25MgF_2$	832	650	2.68	1.42	4.66
$LiF(67)–33MgF_2$	746	947	2.63	1.42	
$NaF(65)–23CaF_2–12MgF_2$	745	574	1.58	1.17	
$LiF(33.4)–49.9NaF_2–17.1MgF_2$	650	860	2.82	1.42	1.15
$LiF(46)–44NaF_2–10MgF_2$	632	858	2.24	1.40	1.20
$Na_2CO_3(56)–44Li_2CO_3$	496	368	2.33	1.85	2.11
$NaCl(50)–50MgCl_2$	450	429	2.24	0.93	0.96
$Li_2CO_3(31)–35K_2CO_3–Na_2CO_3$	397	275	2.31	1.69	2.04
$MgCl_2(63)–22.3NaCl–14KCl$	385	461	2.25	0.96	0.95
$NaCl(7.8)–6.4Na_2CO_3–85.5NaOH$	282	316	2.13	2.51	
LiCl(37)–63LiOH	262	485	1.55	2.40	1.10

Table 8
Melting temperatures, solidification temperatures and heats of fusion some compounds and compositions on the based on nitrates and nitrites [76].

Salt composition, mol.%	T_m, °C	T_{sol}, °C	ΔH_f, J/g
$NaNO_3 \cdot NaOH$	271	213	265
$NaNO_3 \cdot 2NaOH$	270	218	295
$NaNO_3(72)–28NaOH$	247	213	237
$NaNO_3(41)–59NaOH$	266	221	278
$NaNO_3(18.5)–81.5NaOH$	257	254	292
$NaNO_2 \cdot NaOH$	265	228	313
$NaNO_2(80)–20NaOH$	232	232	252
$NaNO_2(27)–73NaOH$	237	227	294

Lithium nitrate

$$C_{ps}(\mathrm{J/g\,K}) = 0.585 + 2.182 \times 10^{-3} T(\mathrm{K}) \quad \text{for } 334 - 493\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 1.681 + 6.389 \times 0^{-4}\, T(\mathrm{K}) \quad \text{for } 540 - 653\,\mathrm{K}$$

Sodium nitrate

$$C_{ps}(\mathrm{J/g\,K}) = 3.15 - 1.186 \times 10^{-2}\, T(\mathrm{K}) + 1.807 \times 10^{-5} (T/\mathrm{K})^2 \quad \text{for } 334 - 493\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 1.676 + 1.282 \times 10^{-5} (T/\mathrm{K}) \quad \text{for } 586 - 653\,\mathrm{K}$$

Potassium nitrate

$$C_{ps}(\mathrm{J/g\,K}) = 0.326 - 1.91\times10^{-3}(T/\mathrm{K}) \quad \text{for } 334-400\,\mathrm{K}$$
$$C_{ps}(\mathrm{J/g\,K}) = 2.442 - 5.682\times10^{-3}\,T(\mathrm{K}) + 6.628\times10^{-6}(T/\mathrm{K})^2 \quad \text{for } 423-600\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 1.417 - 4.678\times10^{-5}(T/\mathrm{K}) \quad \text{for } 620-733\,\mathrm{K}$$

Besides the above-stated nitrates thermal capacities of following rather widespread salt compositions have been determined:

$NaNO_2$–NaOH (27–73 mol.%)

$$C_{ps}(\mathrm{J/g\,K}) = 1.123 + 1.184\times10^{-3}\,T(\mathrm{K}) - 7112.8(T/\mathrm{K})^{-2} \quad \text{for } 334-493\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 2.067 \quad \text{for } 534-573\,\mathrm{K}$$

$NaNO_2$–NaOH (50–50 mol.%)

$$C_{ps}(\mathrm{J/g\,K}) = 1.562 + 4.153\times10^{-4}\,T(\mathrm{K}) - 32,489(T/\mathrm{K})^{-2} \quad \text{for } 334-493\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 1.962 \quad \text{for } 534-573\,\mathrm{K}$$

$NaNO_2$–NaOH (80–20 mol.%)

$$C_{ps}(\mathrm{J/g\,K}) = -5796 + 1444\times10^{-2}\,T(\mathrm{K}) - 257,490(T/\mathrm{K})^{-2} \quad \text{for } 334-413\,\mathrm{K}$$
$$C_{ps}(\mathrm{J/g\,K}) = -31,503 + 4729\times10^{-2}\,T(\mathrm{K}) - 2,438,500(T/\mathrm{K})^{-2} \quad \text{for } 453-503\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 1795 \quad \text{for } 534-573\,\mathrm{K}$$

$NaNO_3$–NaOH (18.5–81.5 mol.%)

$$C_{ps}(\mathrm{J/g\,K}) = -0.200 + 3.277\times10^{-3}T(\mathrm{K}) - 55,743(T/\mathrm{K})^{-2} \quad \text{for } 334-523\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g\,K}) = 2.054 \quad \text{for } 534-573\,\mathrm{K}$$

$NaNO_3\cdot 2NaOH$

$$C_{ps}(\mathrm{J/g\,K}) = -0.330 + 2258\times10^{-3}T(\mathrm{K}) \quad \text{for } 334-513\,\mathrm{K}$$

Results of experimental investigations of thermodynamic properties of some pure salts and compositions on their basis have been above considered. Besides the above-stated properties and other thermophysical properties for designing HSUs, we should possess the data on thermal conductivity and diffusivity both in solid, and in liquid states. Below we will consider results of some experimental studies of these properties.

Tufen et al. [77] investigated heat conductivity of some fused salts and mixes. The spent measurements has yielded following results:

Lithium nitrate

$$\lambda_l(\mathrm{W/m\,K}) = 0.506 - 0.516 \quad \text{for } 320-400\,^\circ\mathrm{C}$$

Potassium nitrate

$$\lambda_l(\mathrm{W/m\,K}) = 0.416 - 0.423 \quad \text{for } 343-427\,^\circ\mathrm{C}$$

Sodium nitrite

$$\lambda_l(\mathrm{W/m\,K}) = 0.528 - 0.530 \quad \text{for } 286-325\,^\circ\mathrm{C}$$

$NaNO_3$–KNO_3 (50–50 mol.%)

$$\lambda_l(\mathrm{W/m\,K}) = 0.458 - 0.460 \quad \text{for } 251-398\,^\circ\mathrm{C}$$

$NaNO_3$–$NaNO_2$–KNO_3 (7–40–53 mol.%)—(HTS-Hitec)

$$\lambda_l(\mathrm{W/m\,K}) = 0.458 - 0.460 \quad \text{for } 251-398\,^\circ\mathrm{C}$$

The error of measurements of heat conductivity is estimated in 4%.

Table 9
Optimal values of the coefficients in Eq. (1) for determination of thermal conductivity of alkali metals chlorides and bromides [78,79].

Salt	λ_m	b	T_m	Temperature range, K
LiCl	0.626	-2.9×10^{-4}	883	967–1321
NaCl	0.519	-1.8×10^{-4}	1074	1170–1441
KCl	0.389	-1.7×10^{-4}	1043	1056–1335
RbCl	0.249	-1.1×10^{-4}	990	1046–1441
CsCl	0.209	-1.2×10^{-4}	918	960–1360
NaBr	0.320	-0.8×10^{-4}	1020	1050–1267
KBr	0.218	-0.4×10^{-4}	1007	1035–1245
RbBr	0.203	-1.1×10^{-4}	953	1031–1326
CsBr	0.149	-0.2×10^{-4}	909	948–1314

Nagasaka et al. [78] used a method of forced Rayleigh scattering for measurement thermal diffusivities of chlorides of alkaline metals in liquid state. Being based on the measured values and using literary data, authors have determined the thermal conductivity. Processing of the calculated values of thermal conductivity by least-squares method has given linear regression temperature dependence of a kind:

$$\lambda_l(\mathrm{W/m\,K}) = \lambda_m + b(T - T_m) \tag{1}$$

Factors in regression equations are presented in Table 9. The error of thermal diffusivity determination by given method has made for LiCl–11%, for NaCl–4%, for KCl–5%, for RbCl–6%, and for CsCl–9%. Most likely, errors of determination of heat conductivity should be expected not less, than for thermal diffusivity.

In following work Nakazawa et al. [79] used the above described method [78] for determination of thermal diffusivity and heat conductivity of melts of alkaline metals bromides. Table 9 illustrates factors in regression equations (1) for heat conductivity. The determination error thermal diffusivity is estimated in 7% for NaBr, 3% for KBr, 7% for RbBr and 11% for CsBr.

Araki et al. [80] have carried out complex investigation of thermophysical properties of melts of some compositions on the basis of alkaline metals carbonates. The density, a thermal capacity and thermal diffusivity are experimentally measured. As samples have been chosen Li_2CO_3–K_2CO_3 (42.7–57.3 mol.%), Li_2CO_3–K_2CO_3 (50–50 mol.%) and Li_2CO_3–K_2CO_3 (62.0–38.0 mol.%). The first and third mixes represent eutectic compositions the melting temperatures of which are equal 498 and 488 °C, respectively. The second mix is not that other, as the compound $LiKCO_3$, which melts at 505 °C. All these compositions are rather stable at the raised temperatures. As a result of measurements are offered following regression correlations:

Li_2CO_3–K_2CO_3 (42.7–53.7 mol.%)

$$a(\mathrm{m^2/s}) = 1.93\times10^{-7} + 4.85\times10^{-10}(T - 771) \quad \text{for } 807-960\,\mathrm{K}$$
$$C_{ps}(\mathrm{J/g}) = 0.592 + 1.16\times10^{-3}T \quad \text{for } 341-634\,\mathrm{K}$$
$$C_{pl}(\mathrm{J/g}) = 1.49 \quad \text{for } 781-1071\,\mathrm{K}$$
$$\rho_l(\mathrm{g/sm^3}) = 2.028 - 0.465(T - 771) \quad \text{for } 819-1065\,\mathrm{K}$$
$$\lambda_l(\mathrm{W/m\,K}) = 0.587 + 1.26(T - 771) \quad \text{for } 807-960\,\mathrm{K}$$

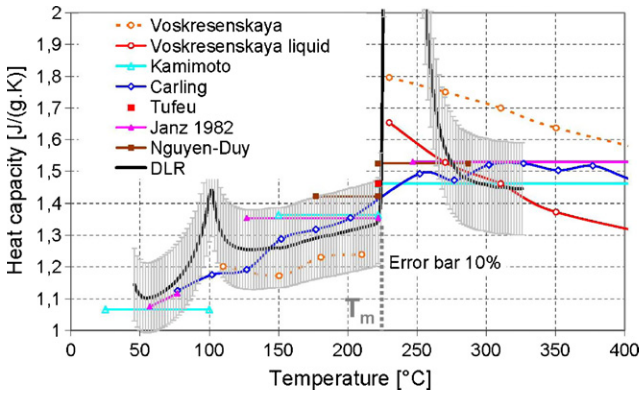


Fig. 2. Heat capacity of eutectic composition KNO_3–$NaNO_3$ obtained with using a differential-scanning calorimeter technique [90].

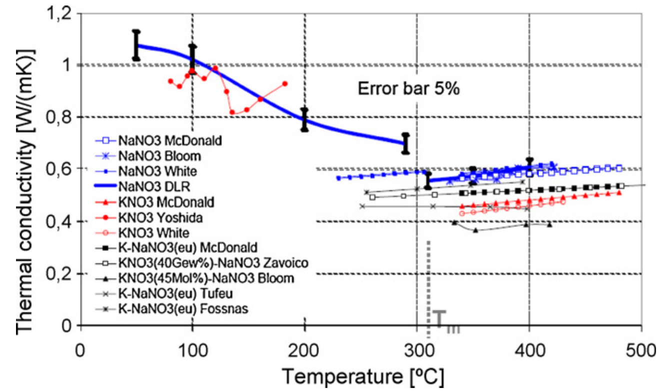


Fig. 4. The temperature dependence of thermal conductivity of some nitrates and their compositions [90].

Li_2CO_3–K_2CO_3 (50–50 mol.%)

$$\begin{aligned}
&a(\mathrm{m^2/s}) = 1.97\times10^{-7} + 4.17\times10^{-10}(T-778) && \text{for } 805-960\,\mathrm{K}\\
&C_{ps}(\mathrm{J/g}) = 0.618 + 1.03\times10^{-3}T && \text{for } 352-626\,\mathrm{K}\\
&C_{pl}(\mathrm{J/g}) = 1.55 && \text{for } 800-1066\,\mathrm{K}\\
&\rho_l(\mathrm{g/cm^3}) = 2.011 - 0.465(T-778) && \text{for } 800-1083\,\mathrm{K}\\
&\lambda_l(\mathrm{W/m\,K}) = 0.617 + 1.10\times10^{-3}(T-778) && \text{for } 805-973\,\mathrm{K}
\end{aligned}$$

Li_2CO_3–K_2CO_3 (62.0–38.0 mol.%)

$$\begin{aligned}
&a(\mathrm{m^2/s}) = 1.92\times10^{-7} + 3.56\times10^{-10}(T-761) && \text{for } 770-979\,\mathrm{K}\\
&C_{ps}(\mathrm{J/g}) = 0.562 + 1.16\times10^{-3}T && \text{for } 770-979\,\mathrm{K}\\
&C_{pl}(\mathrm{J/g}) = 1.60 && \text{for } 773-1071\,\mathrm{K}\\
&\rho_l(\mathrm{g/cm^3}) = 1.991 - 0.434(T-761) && \text{for } 783-1082\,\mathrm{K}\\
&\lambda_l(\mathrm{W/m\,K}) = 0.618 + 0.95\times10^{-3}(T-761) && \text{for } 770-979\,\mathrm{K}
\end{aligned}$$

In 2006, Bauer et al. [81] have presented at the Ecostock 2006 conference the results of measurements of some thermophysical properties of sodium nitrate and equimolar eutectic compositions of KNO_3–$NaNO_3$. Fig. 2 shows the comparison of thermal capacity of the composition, measured on a differential-scanning calorimeter by Bauer et al., and the results obtained by other authors. Within a measurement error all data are coincided with each other. Temperature dependence of thermal diffusivity determined by laser flash method is resulted in Fig. 3. For comparison the data of other authors is presented in the same figure. The greatest divergence is observed for data in solid phase at low temperatures. The most part of measured values of thermal diffusivity in neighborhood of melting point is in the satisfactory consent with each other.

Fig. 4 illustrates the temperature dependence of heat conductivity obtained for some nitrates and their compositions by different researchers. As seen from Fig. 4, heat conductivity of pure sodium and potassium nitrates as well as of their mixes are close to each other.

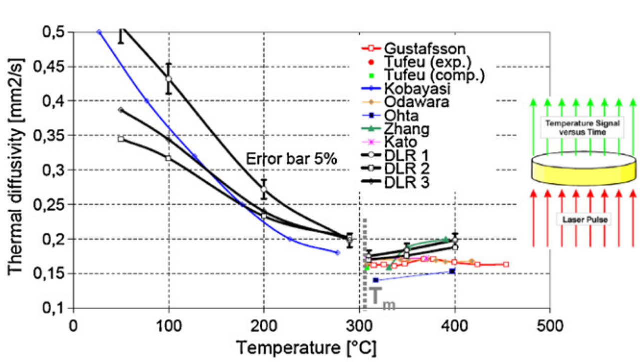


Fig. 3. The temperature dependence of the sodium nitrate thermal diffusivity [90].

2.3. Overcooling of salts and salt compositions

In ideal isothermal (phase change) heat stores, its accumulation and liberation occurs at the same temperature. However in practice at substance solidification the speed of its crystallization is defined by crystal structure, presence of crystallization centers, external conditions of heat exchange etc. In isothermal HSU, it is desirable, that phase change HSM solidified at invariable temperature and provided the steady heat transfer from HSU to the working heat-carrier. The majority of metals possess the ideal curves of fusion and solidification. Unfortunately, many salts are subject to the overcooling phenomenon. Very often the same material overcooling degree can vary over a wide range. For some compositions, the extent of overcooling reaches considerable values (see Table 10). Application of such salts in HSUs reduces their operational characteristics. And in the presence of considerable overcooling, it is at all impossible. Therefore studying the overcooling degrees in perspective HSMs is rather important. And when overcooling takes place in PCMs, it is necessary to take special measures on its prevention.

2.4. Change of volume at fusion of salt HSM

One major property of phase change materials, making considerable impact on design performances of thermal storage devices, is change of their volume at phase transition. The data on studying the temperature dependences of density of salts and their compositions are rather limited in the literature. This circumstance complicates determination of change of volume at fusion. At the

Table 10
Overcooling degree of some fluorides and their composition [53].

Composition, mol.%	Overcooling grade, °C	Composition, mol.%	Overcooling grade, °C
LiF–30MgF$_2$	0	KF	0
LiF–13KF–13MgF$_2$	0	NaF–40MgF$_2$–20CaF$_2$	40–60
NaF–22CaF$_2$–13MgF$_2$	15–30	CaF$_2$–50MgF$_2$	3–20
LiF–20CeF$_3$	0	NaF–60MgF$_2$	70–80
LiF–19.5CaF$_2$	2–3	NaF	0
KF–15CaF$_2$	0	KF–69MgF$_2$	20
KF–15MgF$_2$	0	NaMgF$_3$	30–120
NaF–20MgF$_2$–16KF	20–30	KF–61CaF$_2$	30–40
NaF–32CaF$_2$	30–40	KCaF$_3$	20–30
NaF–23MgF$_2$	60–80	KMgF$_3$	20–30
LiF	0	MgF$_2$–40CeF$_3$	7–20

Table 11
Volume change of some salts at melting.

Salt composition, wt.%	T_m, °C	$\Delta V/V_s$, %	Reference
KNO_3	337	3.3(l)	[30]
KNO_3(54)–46$NaNO_3$	222	4.6(l)	[30]
KNO_3(67)–33$LiNO_3$	133	13.5(l)	[30]
Li_2CO_3(47)–53K_2CO_3	491	3.9(ex)	[44]
LiF	850	45(l)	[82]
LiF(27)–12NaF–55KF–6MgF_2	449	≈30(ex)	[82]
LiF(29)–12NaF–59KF	454	≈30(ex)	[82]
LiF(29)–12NaF–59KF	462	4.5(ex)	[44]
LiF(33)–67KF	492	≈12(ex)	[82]
LiF(33)–67KF	493	4.3(ex)	[44]
$LiKCO_3$	488	9.6(ex)	[82]
$LiNO_3$	254	21.5(l)	[30]
$LiNO_3$(49)–51$NaNO_3$	194	13.0(l)	[30]
LiOH	450	>1(l)	[82]
LiOH	470	2.6(ex)	[82]
LiOH	473	1(ex)	[44]
NaF	1000	28.3(l)	[82]
$NaNO_2$	270	16.5(l)	[30]
$NaNO_3$	306	10.7(l)	[30]

(l), from literature; (ex), experiment.

same time in the literature practically there are no results of direct measurements of changes of volume at fusion high-temperature phase change HSM on the basis of salts and their mixes. We know only the work of Heidenreich and Parekh [44], in which experimental data for four salt compositions are obtained. The data found in the literature are resulted in Table 11. As seen from this table, many salts and compositions undergo considerable changes in volume at the fusion, exceeding 10%. Considerable change of volume at fusion of HSM can promote formation of voids during its solidification and in doing so to lower intensity of heat removal at extraction of heat from the accumulator and to increase charging time of HSU, respectively. Application of such compositions complicates the design of HSU and reduces their efficiency also.

2.5. Long-term characteristics salt HSM (thermal cycling)

In accordance with purpose, the HSU's service life can vary in considerable limits. In devices for space application, their service life can be limited by several months or years. It is supposed that the commercial HSU to be used during 20–30 years. Throughout all period of operation the thermal storage material should have stable characteristics. In the literature, there is not enough information concerning behavior of high-temperature phase change heat storage materials, undergone to repeated cycles of fusion and solidification. Below we will consider some works, in which this problem was studied.

Along with studying thermophysical properties of nine salt compositions, Venkatesetti and LeFrois [58] investigated ternary composition $NaNO_3$–NaCl–Na_2SO_4 (86.3–8.4–5.3 mol.%) and binary eutectic mixture $NaNO_3$–NaOH (70–30 mol.%) concerning to their thermal stability. The specified compositions have been made of chemically pure products. Mixes were placed in containers of mild steel and were exposed continuous thermal cycling between 100 and 350 °C. The heating cycle proceeded 1.5 h. After that the material was maintained at 350 °C within one hour then it was cooled on air during one hour. The total number of thermal cycles was 140. After such processing, the eutectic mix has been powder and then the temperature and heat of fusion with using a differential-scanning calorimeter have been determined. The obtained data with the same data for samples that were not exposed thermal cycling were compared. It is not found changes in melting temperatures; however heat of fusion differed on 2% that is in limits of measurement error. Two hundred thermal cycles of eutectic compositions prepared of technical grades of initial salts, have not an appreciable effect. Within an experiment error, it is not observed the changes in temperature and heat of fusion. After 300 thermal cycles with eutectics of their technical grades of salts, the containers have been cut on three parts. Experimental results on temperature and heat of fusion, received for mixes from all three parts, have not shown any changes. In summary, authors notice, that the binary eutectic is stable up to 400 °C while the ternary eutectic shows good stability to 450 °C.

Similar studies of long-term characteristics of lithium hydroxide and eutectic compositions on the basis sodium hydroxide have been carried out by the American and Japanese researchers. Results of these works will be considered below in Section 2.6.

2.6. Compatibility salt HSM with constructional materials

Along with attractive physical properties, the thermal storage materials should be chemically resistant and not enter chemical interaction with materials of containers, in which they are placed. This problem attracted the attention of many researchers. As it was already specified in Table 6, the HSMs studied by Marianowski and colleagues [46,47] is compatible with the stainless steel. However, any details concerning to test specifications are absent.

Misra and Whittenberger [53] have studied compatibility of some fluorides with constructional alloys on the basis of cobalt, iron, nickel and of some refractory metals. In total, it has been investigated about 30 materials. The eutectic salt compositions (LIF–19.5CaF_2 with melting point 769 °C and NaF–27CaF_2–36MgF_2 with melting point 905 °C) were exposed at the temperature, which exceeded on 25 °C their melting point. The metal to be tested contacted with the salt melt placed in sealed quartz capsule or in an open crucible of alumina in the environment of argon, and was exposed from 50 till 500 h. At the 500-hourly exposition, the minimum depth of corrosion 15–30 μm has been registered for nickel alloys *Hastelloy B* and *N*, and the maximum depth 280 μm for steel *RA-330*. It was not detected the interaction traces between the specified salt compositions and such refractory metals as molybdenum, niobium, tantalum and tungsten.

In other work [54], same researchers have presented the study results of compatibility of constructional alloys with the following eutectic mixes: NaF–22CaF_2–13MgF_2, NaF–32CaF_2 and NaF–23MgF_2. The exposition duration varied from 75 till 100 h. Experiments have shown, that only a few alloys were resistant relating to each mix without any damages. In particular, the mild steel, pure nickel and niobium–zirconium alloy have shown resistance to all to three eutectics. Nickel alloy *Hastelloy B* and stainless steel *SS304* have found out the minimum corrosion in contact with mix NaF–22CaF_2–13MgF_2. Containers of *PH-14-8 and SS304* can be used for mix NaF–32CaF_2, and the container of *Hastelloy N*—for mix NaF–23MgF_2.

Heidenreich and Parekh [44] have studied the compatibility of lithium hydroxide melt with some metals and alloys. Small samples of metals were exposed in the salt placed in individual capsules of *Ni-200* and *Ni-270* within 300 h at temperature 500 °C. Tests have yielded following results:

- *Pure metals*: Pure nickel, zirconium, the titanium and silver have shown the best corrosion resistance, than various alloys on the basis of nickel, chrome and iron. Nickel has shown the least corrosion, and iron had considerable losses of metal.
- *Alloys with the low content of chrome*: Alloys on the basis of nickel and iron containing a small amount of chrome or not half containing it (*Hastelloy B*, *Hastelloy W*, *Incoloy 999*) were less reactive, than alloys with the high maintenance of chrome.
- *Alloys on the basis of zirconium and titanium*: Zirconium and titanium alloys possess relatively low reactionary ability and test insignificant losses after 300 h of exposition at 500 °C.

Faget [83] investigated compatibility LiOH and some fluorides with 20 constructional alloys on the basis of iron, nickel and zirconium. LiOH, LiF and eutectic compositions 12NaF–59KF–29LiF (melting point 454 °C), 33LiF–67KF (492 °C) and 67LiF–33MgF$_2$ (739 °C) have been chosen as the salts to be tested. The container was filled by salt so that it covered the tested sample of an alloy at melting. The container with tested materials exposed at the temperature exceeding the melting point of salt on 27–28 °C within 5 weeks. Results of these tests are resulted below. For a mix 12NaF–59KF–29LiF, the best results have shown alloys *Hastelloy N*, *Hastelloy X*, *Heynes 25*, *Nickel 200*, *Nickel 201* and stainless steels *SS304*, *SS316*. Intensity of corrosion for these alloys varied within 0.17–0.74 μm/year. The least interaction between a mix 33LiF–67KF and the same nickel alloys and corrosion-proof alloys *SS114*, *SS171* was found out. In these tests, speed corrosion is in the range from 0 to 0.56 μm/year. Alloy *Inconel 600* with speed of corrosion 0.70 μm/year has showed the most proof alloy in the relation to lithium hydroxide. In testing the mix 67LiF–33MgF$_2$, the best index had the alloy *Hastelloy N*, for which speed of corrosion was made 2.95 μm/year. Fluoride of lithium reacted least of all with alloys *Armco 18SR* and *Hastelloy* X. Intensity of corrosion of these alloys in LiF has made 0.47 and 0.23 μm/year, respectively.

To meet constructional requirements besides corrosion resistance, the material of the container for isothermal THERE should have comprehensible mechanical and metallurgical properties. The alloy used for the container, should: to be easily processed, be accessible and cheap. Pidkok et al. [84] were guided by these criteria, when for lithium hydroxides they choose nickel *Ni-201*. This material represents commercially accessible pure nickel with the low maintenance of carbon. In laboratory tests, two containers with external diameter 25 mm and height 300 mm with 120 g of lithium hydroxide have been used. Containers have been filled LiOH melt in the atmosphere of argon, and then containers have been sealed by electron beam welding at a room temperature. Containers were undergone to thermal cycles of fusion and solidification with heating period of 58 min and the period of cooling of 36 min. The first container was tested 4700 cycles (7360 h), and the second 2700 cycles (4230 h). The temperature in containers was controlled continuously during all period of tests. Changes in weight and the sizes of containers it is not found out. Temperature curves have not indicated any decomposition or change in the lithium hydroxide composition.

The long-term investigations [85] of phase change materials carried out by the group of researchers from Electrotechnical laboratory in Ibaraki (Japan) have established, that the eutectic compositions on the basis hydroxides of sodium NaOH–NaNO$_3$ (81.5–18.5 mol.%) and NaOH–NaNO$_2$ (73–27 mol.%) are very perspective HSMs. Study of compatibility of these salt mixes with constructional materials was following stage of investigations. The steels produced by Japanese companies were chosen as the objects of studies. Tests were spent at temperature 350 °C in the electric furnace in nitrogen atmosphere. The metals immersed in salt melt which, in turn, were placed in the container with open top. Duration of tests was 100, 350, 1000, 2000 and 4000 h. After the specified period the sample was taken, cleared in the distilled water. Then was weighed and exposed to ultrasonic clearing and it was again weighed. The difference in weight before ultrasonic clearing corresponded with average mechanical hardness of surface products. The cylindrical container was cut in an axial direction to study an internal surface of metal in a zone of interaction with salt. The results received in this work are presented in Table 12. Speed of corrosion has been estimated in results of 4000-h of tests. Carbonaceous steels and steel with the nickel content had the best indicators while stainless steels of marks 304L, 316L, 430 on the resistance to corrosion considerably conceded to the first.

Table 12
Compatibility of steels with NaOH-based compositions [85].

Material	Corrosion rate, mkm/year
NaOH–NaNO$_3$ (81.5–18.5 mol.%)	
JIS G3101 SS41	− 2 to −7
JIS G3101 SB46	+ 2 to + 3
JIS G3101 SB46M	− 7 to − 9
JIS G4103 SCMV4	− 2 to − 3
JIS G4103 SCMV6	+ 2 to + 3
JIS G3127 SL3N28	+ 1 to + 2
JIS G4304 SUS430	− 40 to − 45
JIS G4304 SUS304L	− 80 to −90
JIS G4304 SUS316L	− 80 to − 100
NaOH–NaNO$_2$ (73–27 mol.%)	
JIS G3101 SS41	− 2 to −3
JIS G3101 SB46	− 2 to − 3
JIS G3101 SB46M	− 5 to − 6

The thermal capacity both eutectics have not changed after 4000 h of tests. However the temperature and heat of fusion of blend NaOH–NaNO$_3$ after long tests have undergone minor changes. The melting temperature has decreased on 3–6°, and heat of fusion has dropped on 5% that is a little above an error of measurement of 2% on the differential-scanning calorimeter used by these researchers. After these results it has been decided to conduct 5000-h of test with use of the container of Al$_2$O$_3$. Measured temperature and heat of fusion was same. Authors [85] assumed that these changes are connected not with corrosion, and with small decomposition of nitrate of sodium. The further analysis [86] has confirmed this fact. In the eutectic NaOH–NaNO$_2$, it was not found out changes in temperature and heat of fusion.

In the previous tests [85,86], the salts of chemical pure grade have been used. However in practical applications less pure salts are used. To study the influence of purity of salts Abe et al. [86] have conducted the 10,000-h test of carbonaceous steel *SB46* and three various grades of salts: reagent grade NaOH and reagent grade NaNO$_3$; NaOH produced by ion-exchange membrane technology (99%), and industrial grade (99%) NaNO$_3$; NaOH produced by the asbestos-membrane technology (97%), and industrial grade NaNO$_3$. The specified salts differed, mainly, by content of NaCl as an impurity. Rather appreciable distinctions have been found in thermal properties. The dissolution of metal elements in salts was also observed. As seen from Table 13, the initial values of melting temperatures and heats of fusion differed from each other. In special experiments, it has been found that the increase of sodium chloride content considerably lowers the melting point and heat of fusion. It is easy to notice, that the melting temperature and heat of fusion in all three compositions varied approximately on the same values.

2.7. Cost of salt heat storage materials

All data on cost of salts concern, practically, to the seventieth and eightieth years of last century. So above in Table 6, we have already cited data taken from works of Marianowski and its colleagues [46,47]. Eihelberger and Gillman [43] have also cited the data on cost of fluorides (see Table 14). On the basis of these data,

Table 13
Thermal properties of salts before and after 10,000 h immersion with SB46 [86].

	Reagent NaOH–NaNO$_3$		99% NaOH–99%NaNO$_3$		97% NaOH–99%NaNO$_3$	
	Before	After	Before	After	Before	After
T_m, °C	255.5	254.8	253.3	251.2	248.8	245.2
ΔH_f, J/g	292	280	282	272	276	266

Table 14
Some fluorides price [43].

Salt	Price, US$/kg	Salt	Price, US$/kg
NaF	0.74	SrF_2	50.44
KF	1.46	PbF_2	30.27
MgF_2	0.87–1.71	LiF	5.38
CaF_2	0.12	CuF_2	121.11
BaF_2	1.29	NiF_2	202.22
TiF_4	77.78	CrF_3	1.80
AlF_3	0.39	SnF_2	12.44

and also the future improvement of the ‘‘know-how’’ of fluorides, they have made estimation of cost of 32 fluorides and their compositions. Trunin [33] has presented the prices of some salts made in the USSR. Available in [33,43,46,47] the prices cannot be of course used in estimation of HSM and HSU cost, since they require their corrections for the present moment.

The last data on cost of some salts it is possible to find in [86,87]. Data from these works are shown in Table 15.

2.8. Methods of effective heat conductivity enhancement of thermal storage materials

Above in Section 2.2, it has been shown that the most part of salts, which can be used as heat storage materials, have very low heat conductivity nearby 1 W/m K. Such a low heat conductivity of salts, undoubtedly, is rather essential obstacle for their application in HSUs. We [19] have earlier considered the basic methods of increasing the effective heat conductivity of low temperature materials. Such means as: container ribbing; introducing high conductivity structures into material; impregnation high conductive porous structures by heat storage materials are used to achieve the specified purpose. All these methods are used in low temperature HSUs. It seems that the use of graphite fibers or expanded graphite with extremely high heat conductivity is the perspective direction to enhance conductivity of high-temperature salts.

Employees of the German space centre (DLR) Tamme et al. [89,90] have carried out investigations of influence of introducing the graphite structures into compositions on the basis of nitrates of lithium, sodium and potassium. So, composition PCM-1 represents the eutectic mix KNO_3–$LiNO_3$ (68:32 wt.%) with melting temperature 133 °C, PCM-2 consists of the eutectic mix KNO_3–$NaNO_3$ (54:46 wt.%) with melting temperature 222 °C. In total, it has been investigated five samples of graphite consisting compositions. Samples have been made by three methods. The sample of the first type has been obtained by infiltration of salt melt into porous structure of expanded graphite. Cold pressed samples have been obtained by a method of cold pressing at a room temperature of

Table 15
Price of some nitrates and carbonates.

Salt	Price, US$/kg	Reference
$NaNO_3$ (technical grade)	0.41	[87]
$NaNO_3$	0.20	[88]
KNO_3 (technical grade)	0.62	[87]
KNO_3	0.30	[88]
$Ca(NO_3)_2$ (technical grade)	1.43	[87]
Hitec (40$NaNO_2$–7$NaNO_3$–53KNO_3)	1.92	[87]
Solar Salt (60$NaNO_3$–40KNO_3)	0.49	[87]
$Ca(NO_3)_2$ (42)–15$NaNO_3$–43KNO_3	1.19	[87]
KOH	1.00	[88]
NaCl	0.15	[88]
Na_2CO_3	0.20	[88]
K_2CO_3	0.60	[88]

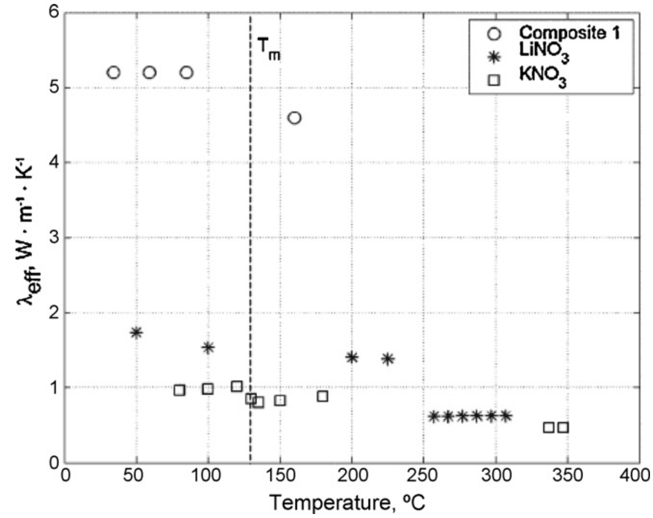


Fig. 5. The effective thermal conductivity of graphite-content composition on the basis of KNO_3–$LiNO_3$ (68:32 wt.%) [91].

salt PCM-2 and flakes of ground expanded graphite. The ratio of salt and graphite was 80:20 on volume. Hot pressed samples differed from cold pressed only that they were pressed at temperature 180 °C. Measurement of effective heat conductivity carried out with using a stationary method of comparison. The experimental device calibrated on a standard material. The measured results are presented in Figs. 5 and 6. In the same place for comparison, the results of measurement of heat conductivity of nitrates of lithium, potassium and sodium are plotted. Fig. 6 shows that the introduction of expanded graphite in salts has raised the effective heat conductivity, at least, five times.

Similar experiments have been fulfilled by employees of Perpignan University (France) Pincemin et al. [91]. In experiments, three types of the industrial graphite received from TIMCAL and SGL companies have been used. Measurements have been made by a stationary method of comparison. The error of measurements of heat conductivity is estimated in 10%. The obtained results are shown in Figs. 7 and 8. The influence of graphite content can be seen in Fig. 7 where the effective heat conductivity of compositions

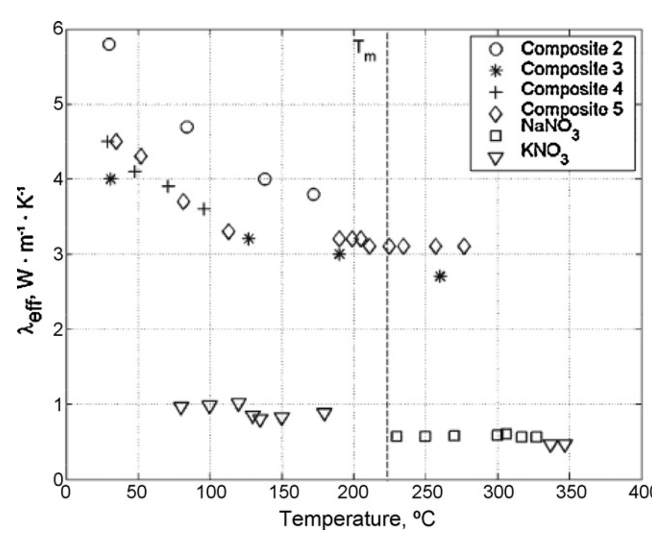


Fig. 6. The effective thermal conductivity of graphite-content composition on the basis of KNO_3–$NaNO_3$ (54:46 wt.%) [91].

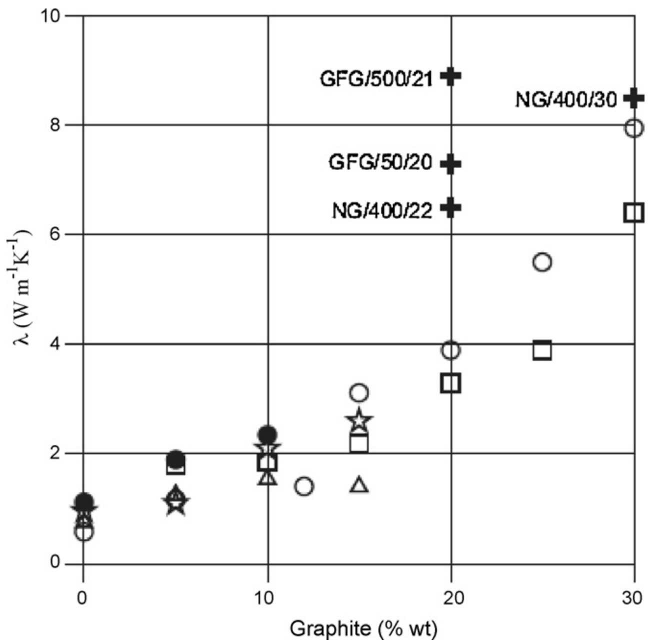


Fig. 7. Thermal conductivities of salts, eutetics and compositions at room temperature: $NaNO_3$ (△), KNO_3 (☆), $NaNO_3/KNO_3$ (laboratory grade) (●), $NaNO_3/KNO_3$ (industrial grade) (○), $ZnCl_2$ (industrial grade) (□), industrial composites made by SGL (+).

at room temperature is presented. Temperature dependence of heat conductivity of the studied compositions is shown in Fig. 8. From these drawings, it is seen that for essential increase of the effective heat conductivity, the compositions have to contain at least 20% of graphite. In addition to these experiments, influence of thermal cycling on thermal storage properties of compositions has been studied. Measurements of heat of fusion after 200 cycles of melting and solidification have found out decrease from 5% to 28% depending on samples. Insignificant decrease and in melting temperature of fusion of compositions was observed also. The

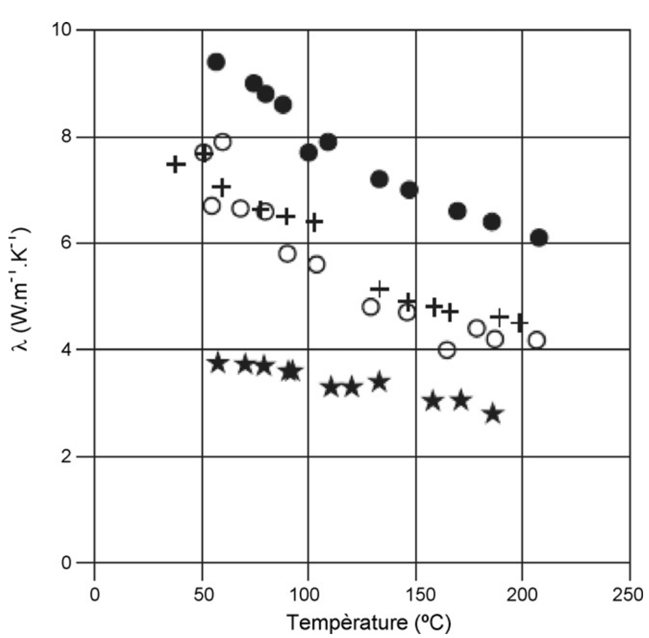


Fig. 8. Thermal conductivities of $NaNO_3/KNO_3$/graphite composites vs temperature: SFG/75/5 (★), NG/400/22 (○), SFG/75/30 (+), GFG/500/21 (●).

reasons which have entailed deterioration of characteristics of compositions have not been established.

2.9. Experimental investigations of pre-production models of high-temperature salt HSUs

Above we have practically considered all stages previous laboratory or pre-production models of high-temperature heat storage devices. Among set of potential materials for heat storage presented in Tables 2–5, rather limited quantity of compositions was is studied at all previous stages. As far as we know, only one group of researchers of Electrotechnical laboratory in Ibaraki (Japan) has carried out all cycles of studies and tests before to start the creation of an experimental sample of HSU.

As Abe et al. [85] noted, despite satisfactory static tests for compatibility in the course of repeated thermal cycling, there can be erased the serious problems between the salt and other parts HSU, such as the places of welding, bends, gaps. And to have the similar information and the information on heat exchange process at charges and discharges of HSUs, in this laboratory, the experimental sample HSU with capacity 30 kWh has been developed. In the process of designing HSU, two serious problems have been considered:

1. In order to avoid a problem connected with considerable change of volume at phase transition, heating of salt in the course of charging should be made from the top, and cooling in the course of discharge from the bottom.
2. Heat exchange pipes should be constant immersed in salt to prevent their finding on a salt interface. From the electrochemical point of view, the moving front of phase interface in the course of melting or solidification can present considerable threat.

The basic parameters of the experimental HSU with taking into account the noted aspects are presented in Table 16.

2.10. Perspective fields of application of high-temperature salt HSUs

Above we already considered the work of Tamme et al. [30] in which the perspective areas in industry and power engineering was noted. Last years the big attention is given to development of Stirling engines (or engines of external combustion). Therefore, it is interesting Schröder's offer [55] to use fluorides of alkaline metals for heat accumulation in Stirling engines. In particular, lithium fluoride was considered as HSM for Stirling engine in the work of Asselman [93].

Table 16
Specification of 30 kWh storage unit [85].

Structure	Horizontal U-tube
Storage capacity	30–35 kWh
Tube size	25.4 mm outer diameter
	2 mm thickness
	600 mm straight length
Tube arrangement	Triangle
	40 mm pitch
	61 U-tubes
	Minimum radius of curvature 38 mm
Heat transfer area	4.65 m^2
Shell size	600 mm inner diameter
	905 mm length
Channel size	600 mm inner diameter
	324 mm
Material	Shell JIS G3103 SB42
	Tube JIS G3461 STB35
	Tube sheet JIS G3201 SF45A

Abe et al. [60,85,86,92] have suggested to use eutectic compositions on the basis sodium hydroxide for daily accumulation of heat on nuclear power plants in off-peak time to use it during peak loading. In view of a wide circulation last years small generating power stations at the separate enterprises, application of HSU as consider Abe et al. [92], will allow to raise efficiency of such generating systems.

A number of the American researchers [39,44,53,54,84,94,95] studied heat storage devices with phase change salt compositions from the point of view of their suitability for work onboard orbital space vehicles as a part of the power installations working on organic Rankin cycle, closed Brighton cycle and Stirling cycle.

Besides the above-stated possible scopes high-temperature phase change HSM, possibility of their application in HSUs of solar thermal power stations [39,46,47,58,87,88,96–104] more often is mentioned. Solar thermal power plants existing till 1990 (STPP) with thermal storage systems have been summarized in [88,104]. If early projects STPP used oil, both as heat storage and as the heat-carrier later projects use already salt compositions. Thus oil cost made 42% of the HSU cost. The review of the works [88] published after 1990, has shown, that the overwhelming majority of developing HSUs for STPP are based on application of salt compositions, both for heat accumulation, and for their use as heat-carriers. All last project of HSUs provide practically the application of eutectic compositions of nitrates.

3. Metal alloys

Above we saw that salts have a set of lacks limiting their application. Among there are low heat conductivity, corrosion activity, the big change in volume at melting, considerable overcooling and high cost of some salts. Metals, as a rule, are deprived those lacks which are characteristic for salts. Despite the lower density of heat storage, in comparison with salts, metals in some cases can compete with the first.

Most likely, Birchenal and Telkes [105] were the first who have analyzed possibility to store the thermal energy by using the heat fusion of metals. Making a start from that work Birchenall and Riechman [73] have undertaken studying of some metal eutectic alloys. Thermal properties of alloys were determined by a differential-scanning calorimeter (DSC) and differential-thermal analysis (DTA). The composition of alloys were taken from the literature. Initial metals were alloyed in graphite crucible. The eutectic composition proved to be true by optical metallography. Experimental installations were preliminary calibrated by means of pure metals. The measurement error of DTA is 4% for heat of fusion and 3 K for melting temperature. For DSC the measurement error was 2% and 1 K, accordingly. Thermal properties of the studied alloys are presented in Table 17.

Table 17
Thermal properties of some metallic eutectic alloys [31].

Alloys (wt.%)	Melting temperature, °C	Heat of fusion, J/g
46.3Mg–53.7Zn	340	185
96Zn–4Al	381	138
34.65Mg–65.35Al	497	285
60.8Al–33.2Cu–6.0Mg	506	365
64.1Al–5.2Si–28Cu–2.2Mg	507	374
68.5Al–5.0Si–26.5Cu	525	364
64.3–34.0Cu–1.7Sb	545	331
66.92Al–33.08Cu	548	372
83.14Al–11.7Si–5.16Mg	555	485
87.76Al–12.24Si	557	498
46.3Al–4.6Si–49.1Cu	571	406
86.4Al–9.4Si–4.2Sb	471	471

Table 18
Thermophysical properties of some new alloys [106].

Composition, wt.%	T_m, °C	ΔH_f, J/g	ρ, g/cm^3	C_{ps}, J/g K	C_{pl}, J/g K
Zn(52)–48Mg	340	180			
Mg(55)–28–17Zn	400	146	2.26		
Al(59)–35Mg–6Zn	443	310	2.38	1.63	1.46
Mg(60)–25Cu–15Zn	452	254	2.80		
Mg(52)–25Cu–23Ca	453	184	2.00		
Al(54)–22Cu–18Mg–6Zn	520	305	3.14	1.51	1.13
Al(65)–30Cu–5Si	571	422	2.73	1.30	1.20
Zn_2Mg	588	230			
Zn(49)–45Cu–6Mg	703	176	8.67	0.42	
Cu (91)–9P	715	134	5.60		
Cu(69)–17Zn–14P	720	368	7.00		
Cu(74)–19Zn–7Si	765	125	7.17		
Cu(56)–27Si–17Mg	770	420	4.15	0.75	
Mg(84)–16Ca	790	272	1.38		
Mg(47)–38Si–15Zn	800	314			
Cu(80)–20Si	803	197	6.60	0.50	
Cu(83)–10P–7Si	840	92	6.88		
Mg_2Cu	841	243			
Si(49)–30Mg–21Ca	865	305	2.25		
Si(56)–44Mg	946	757	1.90	0.79	

Table 19
Thermal properties of some metallic alloys [31].

Alloys (wt.%)	Melting temperature, °C	Heat of fusion, J/g
46.3Mg–53.7Zn	340	185
96Zn–4Al	381	138
34.65Mg–65.35Al	497	285
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64.1Al–5.2Si–28Cu–2.2Mg	507	374
68.5Al–5.0Si–26.5Cu	525	364
64.3–34.0Cu–1.7Sb	545	331
66.92Al–33.08Cu	548	372
83.14Al–11.7Si–5.16Mg	555	485
87.76Al–12.24Si	557	498
46.3Al–4.6Si–49.1Cu	571	406
86.4Al–9.4Si–4.2Sb	471	471

Five years after Farkas and Birchenall [106] have published results of determination of thermophysical properties of some new alloys. The obtained results are presented in Table 18.

Gasanaliev and Gamataeva [31], analyzing heat storage properties of various melts, have also specified the perspectives of using the metal alloys for heat accumulation. Table 19 illustrates compositions on the basis of the metal alloys, borrowed from this work.

Wang et al. [107] from Beijing Tsinghua University have developed and investigated two compositions on the basis of aluminum and silicon. First alloy $AlSi_{12}$ contained 12 wt.% of silicon and the second alloy $AlSi_{20}$ with 20 wt.% of silicon. Alloy $AlSi_{12}$ had temperature of fusion 576 °C and heat of fusion 560 J/g, and alloy AlSi20 585 °C and 460 J/g, respectively. Owing to the best properties, the alloy $AlSi_{12}$ has been chosen for the further studies. Thermophysical properties of this alloy are given in Table 20. The alloy $AlSi_{12}$ has been used to develop and test a high-temperature isothermal electric heater intended for thermal energy storage at night, when the tariff for the electric power essentially lower.

Table 20
Thermophysical properties of $AlSi_{12}$ alloy [107].

Property	Unit	Value
Heat capacity of solid	J/g K	1.038
Heat capacity of liquid	J/g K	1.741
Temperature of phase transition	°C	576
Heat of fusion	J/g	560
Density	g/cm^3	2.70
Thermal conductivity	W/m K	160

Table 21
The melting temperature range of investigated storage alloy after repeated thermal cycles [108].

Number of cycles	Phase transition temperature range, °C
0	450.31–455.68
50	450.33–454.27
500	448.55–452.78
1000	447.25–450.38

Table 22
Corrosion results obtained by gravimetric analysis after 1000 thermal cycles[a].

Sample	Mass loss, mg/cm^2	Corrosion rate, mg/day	Corrosion effect
Stainless steel	7.2158	0.0829	Resistant
Carbon steel	9.4210	0.0953	Slightly corroded

[a] The alloy was assumed to have only one thermal cycling per day.

Sun et al. [108] investigated one of ternary eutectic alloys on the basis of the aluminum, offered by Farkas and Birchenall, Al (60 wt.%)–34Mg–6 Zn. In this work, the compatibility of the specified alloy with such constructional materials as stainless steel SS304L and carbonaceous steel C20 is investigated. Besides of this, the behavior of thermal properties of the alloy depending on number of thermal cycles of melting and solidification is studied. Investigated metal samples immersed into a capsule with ternary alloys, which has been placed in a crucible of stainless steel. The crucible with samples has been undergone of thermal cycling between 442 and 455 °C. The duration of one cycle of melting and solidification was 34 min. This procedure has been spent 1000 times. Testing has shown following results.

Measurement of thermal properties has been fulfilled using DSC technique. Dynamics of change of melting temperature of the alloy is presented in Table 21. As it can be seen in this table, the interval of melting temperature changes from −0.02 to −1.41 °C after 50 cycles, from −1.76 to −2.9 °C after 500 cycles and from −3.06 to −5.3 °C after 1000 cycles. It is seen, that the considerable change in melting temperature of the alloy is not observed. Unlike melting temperature, the heat of fusion tends more essential decrease: −0.13% after 50 cycles −7.46% after 500 cycles and −10.98%. The reason of so considerable decrease in heat of fusion is not established.

The results of gravimetric analysis are given in Table 22. Corrosion layers on the carbonaceous steel had non-uniform structure. The corrosion layers, generated on the stainless steel surface, had homogeneous structure and their thickness was thinner, than thickness of layers on the carbonaceous steel. The stainless steel SS304L containing as the basic components Cr, Ni and Ti can be used as the suitable constructional material for the metallic alloy Al–34Mg–6Zn.

4. Conclusions

The present review does not claim to be exhaustive in the high-temperature phase change HSMs. Nevertheless we have tried to consider the state of art of investigations and developments in this area of knowledge. The above-mentioned analysis allows us to do some important conclusions:

1. The hundreds of perspective compositions and materials on the basis of inorganic salts and metal alloys for latent heat storage in the range of temperatures from 120 to 1000 °C have been found out by efforts of many generations of materials researchers.
2. However, before perspective materials will be used in concrete commercial heat storage units, they should pass a long way of studying their physical, chemical properties.
3. Only insignificant number of known perspective materials are provided by reliable thermophysical properties.
4. Data on chemical compatibility of perspective HSM with constructional materials are rather limited.
5. The insufficient attention is paid to study the thermal stability (thermal cycling) of phase change materials during the operating life time.
6. Material cost is the considerable part of expenses in phase change heat storage units. However, the analyses devoted the cost of salts and alloys taking into account the modern state of their manufacture technologies are absent.
7. The basic lack of salts is their low heat conductivity. The insufficient attention is also paid for solving this problem. The use of graphite-content salt compositions is rather promising. However, the introduction of graphite structures into salt mixes should not lead to decreasing their thermal stability.
8. Despite a considerable quantity of studies devoted to studying the salt mixes, a few compositions only have passed all cycles of testing and examinations to be necessary for producing as a commercial product (see Fig. 1). To carry out the whole complex of studies and tests, it is necessary long time and efforts of experts of various profiles. Hence, the coordination of activity of researchers, as in the frame of one country, and internationally is necessary.
9. It seems that the use of phase change metal alloys for heat storage is underestimated by researchers though they are deprived many lacks which are characteristic for salts.
10. The well studied phase change materials cannot be used in isothermal HSUs if the processes of heat transfer between a heats storage capsule and the heat-carrier will be not studied in a sufficient measure. Therefore, the corresponding studies of heat exchange in heat storage structures are necessary.

Acknowledgements

In summary, the author expresses gratitude Prof. William J. Atherton from Cleveland State University (USA) for the help in preparation of materials for present work.

Appendix A. Information on the author

Murat Kenisarin was born in 27 May 1945 in Tashkent, Uzbekistan. He graduated from Thermal Power Engineering Faculty of the Moscow Power Engineering Institute (Russia) in 1969.

In 1972 he finished his studies at the post-graduated courses in the Institute for High Temperatures (USSR Academy of Sciences), Moscow-IVTAN. In 1975 he defended his doctoral thesis at IVTAN, Moscow.

1972–1994 he worked at Physical-Technical Institute and Thermophysical Department of Uzbekistan Academy of Sciences.

1994–2008 he is Deputy of Director General of the Academasbob Scientific & Production Association (Uzbekistan Academy of Sciences). At present he is senior researcher at the same Institute.

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